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<b>(21) International Application Number:</b> PCT/EP99/04656  <b>(22) International Filing Date:</b> 5 July 1999 (05.07.99)  <b>(30) Priority Data:</b> 1442/98                      7 July 1998 (07.07.98)                      CH  <b>(71) Applicant (for all designated States except AT US):</b> NOVARTIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).  <b>(71) Applicant (for AT only):</b> NOVARTIS-ERFINDUNGEN VERWALTUNGSGESELLSCHAFT M.B.H. [AT/AT]; Brunner Strasse 59, A-1230 Vienna (AT).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> ARSLAN-BIR, Martine [FR/FR]; 2, chemin de l'Esp, F-68220 Hegenheim (FR).  <b>(74) Agent:</b> BECKER, Konrad; Novartis AG, Corporate Intellectual Property, Patent & Trademark Dept., CH-4002 Basel (CH).	<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> PESTICIDAL COMPOSITION COMPRISING EMAMECTIN  <b>(57) Abstract</b>  <p>The invention accordingly relates to a composition for the control of insects or representatives of the order <i>Acarina</i>, which is characterised in that it contains a quantitatively variable combination of emamectin in free form or in salt form, as well as <i>inter alia</i> one or more of the compound: Aldicarb; Azinphos-methyl; Benfuracarb; Bifenthrin; Buprofezin; Carbofuran; Carbosulfan; Cartap; Chlorfluazuron; Chlorpyrifos; Cyfluthrin; Lambda-Cy-halothrin; Alpha-cypermethrin; zeta-Cypermethrin; Deltamethrin; Diflubenzuron; Endosulfan; Ethiofencarb; Fenitrothion; Fenobucarb; Fenvalerate; Formothion; Methiocarb; Heptenophos; Imidacloprid; Isoprocarb; Methamidophos; Methomyl; Mevinphos; Parathion; Parathion-methyl; Phosalone; Pirimicarb; Propoxur; Teflubenzuron; Terbufos; Triazamate; Fenobucarb; Tebufenozide; Fipronil; beta-Cyfluthrin; Silafluofen; Fenpyroximate; Pyridaben; Fenazaquin; Pyriproxyfen; Pyrimidifen; Nitenpyram; NI-25; Acetamiprid; Avermectin; an insect-active extract from a plant; a preparation containing insect-active nematodes; a preparation obtainable from <i>Bacillus subtilis</i>; Azinphos A; Azinphos M; Azocyclotin; Bendiocarb; Bensultap; Betacyfluthrin; BPMC; Tebufenpyrad; Tebupirimphos; Tefluthrin; Temephos; Terbam; Tetrachlor-vinphos; Thiafenox; Thiodicarb; or Spinosad, in free form or in salt form, and at least one excipient; a process for the control of pests, a process for the preparation of the composition, the use thereof and the plant propagation material treated therewith, as well as the use of emamectin in the preparation of the composition.</p>		

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Pesticidal composition comprising emamectin

The present invention relates to a composition which contains a combination of pesticidal active ingredients, consisting of emamectin (A) and at least one further pesticidally active compound, a process for the control of pests with this composition, a process for the preparation of the composition, its usage and the plant propagation material thus treated, as well as the use of emamectin and compounds (1) to (185) below in the preparation of the composition.

In literature, certain mixtures of active ingredients have been proposed for pest control. However, the biological properties of these mixtures of known compounds are not fully satisfactory in the field of pest control, for which reason, there is a need to provide further mixtures with synergistic pest-controlling properties, especially for the control of insects and representatives of the order *Acarina*. This problem is solved according to the invention by the preparation of the present composition.

The invention accordingly relates to a composition for the control of insects or representatives of the order *Acarina*, which is characterised in that it contains a quantitatively variable combination of emamectin (A) in free form or in salt form, as well as one or more of the compounds:

- |                           |                     |
|---------------------------|---------------------|
| (2) Aldicarb;             | (16) Deltamethrin;  |
| (3) Azinphos-methyl;      | (17) Diflubenzuron; |
| (4) Benfuracarb;          | (18) Endosulfan;    |
| (5) Bifenthrin;           | (19) Ethiofencarb;  |
| (6) Buprofezin;           | (20) Fenitrothion;  |
| (7) Carbofuran;           | (21) Fenobucarb;    |
| (8) Carbosulfan;          | (22) Fenvalerate;   |
| (9) Cartap;               | (23) Formothion;    |
| (10) Chlorfluazuron;      | (24) Methiocarb;    |
| (11) Chlorpyrifos;        | (25) Heptenophos;   |
| (12) Cyfluthrin;          | (26) Imidacloprid;  |
| (13) Lambda-Cy-halothrin; | (27) Isoprocarb;    |
| (14) Alpha-cypermethrin;  | (28) Methamidophos; |
| (15) zeta-Cypermethrin;   | (29) Methomyl;      |

- (30) Mevinphos;
- (31) Parathion;
- (32) Parathion-methyl;
- (33) Phosalone;
- (34) Pirimicarb;
- (35) Propoxur;
- (36) Teflubenzuron;
- (37) Terbufos;
- (38) Triazamate;
- (39) Fenobucarb;
- (40) Tebufenozide;
- (41) Fipronil;
- (42) beta-Cyfluthrin;
- (43) Silafluofen;
- (44) Fenpyroximate;
- (45) Pyridaben;
- (46) Fenazaquin;
- (47) Pyriproxyfen;
- (48) Pyrimidifen;
- (49) Nitenpyram;
- (50) NI-25, Acetamiprid;
- (51) Avermectin;
- (52) an insect-active extract from a plant;
- (53) a preparation which contains insect-active nematodes;
- (54) a preparation obtainable from *Bacillus subtilis*;
- (55) a preparation which contains insect-active fungi;
- (56) a preparation which contains insect-active viruses;
- (57) AC 303 630;
- (58) Acephat;
- (59) Acrinathrin;
- (60) Alanycarb;
- (61) Alphamethrin;
- (62) Amitraz;
- (63) AZ 60541;
- (64) Azinphos A;
- (65) Azinphos M;
- (66) Azocyclotin;
- (67) Bendiocarb;
- (68) Bensultap;
- (69) Betacyfluthrin;
- (70) BPMC;
- (71) Brofenprox;
- (72) Bromophos A;
- (73) Bufencarb;
- (74) Butocarboxim;
- (75) Butylpyridaben;
- (76) Cadusafos;
- (77) Carbaryl;
- (78) Carbopheno-thion;
- (79) Chloethocarb;
- (80) Chlorethoxyfos;
- (81) Chlormephos;
- (82) Cis-Res-methrin;
- (83) Clopythrin;
- (84) Clofentezin;
- (85) Cyanophos;
- (86) Cycloprothrin;
- (87) Cyhexatin;
- (88) Demeton M;
- (89) Demeton S;
- (90) Demeton-S-methyl;

- |                       |                           |
|-----------------------|---------------------------|
| (91) Dichlofenthion;  | (124) Lambda-cyhalothrin; |
| (92) Dicliphos;       | (125) Malathion;          |
| (93) Diethion;        | (126) Mecarbam;           |
| (94) Dimethoat;       | (127) Mesulfenphos;       |
| (95) Dimethylvinphos; | (128) Metaldehyd;         |
| (96) Dioxathion;      | (129) Metolcarb;          |
| (97) Edifenphos;      | (130) Milbemectin;        |
| (98) Esfenvalerat;    | (131) Moxidectin;         |
| (99) Ethion;          | (132) Naled;              |
| (100) Ethofenprox;    | (133) NC 184;             |
| (101) Ethoprophos;    | (134) Omethoat;           |
| (102) Etrimphos;      | (135) Oxamyl;             |
| (103) Fenamiphos;     | (136) Oxydemethon-methyl; |
| (104) Fenbutatinoxid; | (137) Oxydeprofos;        |
| (105) Fenothiocarb;   | (138) Permethrin;         |
| (106) Fenpropathrin;  | (139) Phenthoat;          |
| (107) Fenpyrad;       | (140) Phorat;             |
| (108) Fenthion;       | (141) Phosmet;            |
| (109) Fluazinam;      | (142) Phoxim;             |
| (110) Flucycloxuron;  | (143) Pirimiphos M;       |
| (111) Flucythrinat;   | (144) Pirimiphos A;       |
| (112) Flufenoxuron;   | (145) Promecarb;          |
| (113) Flufenprox;     | (146) Propaphos;          |
| (114) Fonophos;       | (147) Prothiofos;         |
| (115) Fosthiazat;     | (148) Prothoat;           |
| (116) Fubfenprox;     | (149) Pyrachlophos;       |
| (117) HCH;            | (150) Pyrada-phenthion;   |
| (118) Hexaflumuron;   | (151) Pyresmethrin;       |
| (119) Hexythiazox;    | (152) Pyrethrum;          |
| (120) Iprobenfos;     | (153) RH 5992;            |
| (121) Isofenphos;     | (154) Salithion;          |
| (122) Isoxathion;     | (155) Sebufos;            |
| (123) Ivermectin;     | (156) Sulfotep;           |

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|---------------------------|--|
| (157) Sulprofos;          | (172) Triazuron;                         |
| (158) Tebufenpyrad;       | (173) Trichlorfon;                       |
| (159) Tebupirimphos;      | (174) Triflumuron;                       |
| (160) Tefluthrin;         | (175) Trimethacarb;                      |
| (161) Temephos;           | (176) Vamidothion;                       |
| (162) Terbam;             | (177) Xylylcarb;                         |
| (163) Tetrachlor-vinphos; | (178) YI 5301/5302;                      |
| (164) Thiafenox;          | (179) Zetamethrin;                       |
| (165) Thiodicarb;         | (180) DPX-MP062;                         |
| (166) Thiofanox;          | (181) RH-2485;                           |
| (167) Thionazin;          | (182) D 2341;                            |
| (168) Thuringiensin;      | (183) XMC (3,5,-Xy-lyl Methylcarbamate), |
| (169) Tralomethrin;       | (184) Chlorfenapyr; or                   |
| (170) Triarthen;          | (185) Spinosad,                          |
| (171) Triazophos;         |  |

in free form or in salt form, and at least one excipient.

Enamectin is a mixture of 4"-deoxy-4"-N-methylamino avermectin B<sub>1a</sub>/B<sub>1b</sub> and is described in US-P-4,4874,749 and as MK-244 in Journal of Organic Chemistry, Vol. 59 (1994), 7704-7708. Salts of emamectin that are especially valuable agrochemically are described in US-P-5,288,710.

Compounds (1) to (185) are known to persons skilled in the art; they are mentioned in The Pesticide Manual, 9<sup>th</sup>Ed. (1991), or 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London. They are known for example from the following:

- (1) 2-Methyl-2-(methylthio)propionaldehyde O-methylcarbamoyloxime (Aldicarb), from The Pesticide Manual, 9<sup>th</sup> Ed. (1991), The British Crop Protection Council, London, page 16;
- (2) S-3,4-dihydro-4-oxo-1,2,3-benzotriazin-3-ylmethyl O,O-dimethyl phosphorodithioate (Azinphos-methyl), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 46;
- (3) Ethyl N-[2,3-dihydro-2,2-dimethylbenzofuran-7-yloxycarbonyl(methyl)aminothio]-N-isopropyl-β-alaninate (Benfuracarb), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 57;

- (4) 2-Methylbiphenyl-3-ylmethyl (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (Bifenthrin), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 73;
- (5) 2-tert-Butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazine-4-one (Buprofezin), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 105;
- (6) 2,3-Dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate (Carbofuran), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 126;
- (7) 2,3-Dihydro-2,2-dimethylbenzofuran-7-yl (dibutylaminothio)methylcarbamate (Carbosulfan), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 129;
- (8) S,S'-(2-Dimethylaminotrimethylene) bis(thiocarbamate) (Cartap), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 132;
- (9) 1-[3,5-Dichloro-4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenyl]-3-(2,6-difluorobenzoyl)-urea (Chlorfluazuron), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 143;
- (10) O,O-Diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (Chlorpyrifos), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 166;
- (11) (RS)- $\alpha$ -cyano-4-fluoro-3-phenoxybenzyl (1RS)-cis-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (Cyfluthrin), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 198;
- (12) Mixture of (S)- $\alpha$ -cyano-3-phenoxybenzyl Z-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate and (R)- $\alpha$ -cyano-3-phenoxybenzyl Z-(1S)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate (Lambda-cyhalothrin), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 203;
- (13) Racemate consisting of (S)- $\alpha$ -cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (R)- $\alpha$ -cyano-3-phenoxybenzyl (1S)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (Alpha-cypermethrin), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 210;
- (14) A mixture of (S)- $\alpha$ -cyano-3-phenoxybenzyl (1RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (S)- $\alpha$ -cyano-3-phenoxybenzyl (3RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (zeta-cypermethrin), from The

- Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 265;
- (15) (S)- $\alpha$ -cyano-3-phenoxybenzyl(1R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-carboxylate (Deltamethrin), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 232;
- (16) (4-Chlorophenyl)-3-(2,6-difluorobenzoyl)urea (Diflubenzuron), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 281;
- (17) (1,4,5,6,7,7-Hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene) sulphite (Endosulfan), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 332;
- (18)  $\alpha$ -ethylthio-o-tolyl methylcarbamate (Ethiofencarb), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 343;
- (19) O,O-dimethyl O-4-nitro-m-tolyl phosphorothioate (Fenitrothion), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 369;
- (20) 2-sec-butylphenyl methylcarbamate (Fenobucarb), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 371;
- (21) (RS)- $\alpha$ -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate (Fenvalerate), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 388;
- (22) [Formyl(methyl)carbamoylmethyl] O,O-dimethyl phosphorodithioate (Formothion), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 440;
- (23) 4-Methylthio-3,5-xylol methylcarbamate (Methiocarb), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 677;
- (24) 7-Chlorobicyclo[3.2.0]hepta-2,6-dien-6-yl dimethylphosphate (Heptenophos), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 467;
- (25) (6-Chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidenamine (Imidacloprid), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 491;
- (26) 2-Isopropylphenyl methylcarbamate (Isoprocarb), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 504;
- (27) O,S-dimethyl phosphoramidodithioate (Methamidophos), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 563;



- (28) S-methyl N-(methylcarbamoyloxy)thioacetimidate (Methomyl), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 570;
- (29) Methyl 3-(dimethoxyphosphinoyloxy)but-2-enoate (Mevinphos), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 592;
- (30) O,O-diethyl O-4-nitrophenyl phosphorothioate (Parathion), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 648;
- (31) O,O-dimethyl O-4-nitrophenyl phosphorothioate (Parathion-methyl), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 650;
- (32) S-6-chloro-2,3-dihydro-2-oxo-1,3-benzoxazol-3-ylmethyl O,O-diethyl phosphorodithioate (Phosalone), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 674;
- (33) 2-Dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (Pirimicarb), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 690;
- (34) 2-Isopropoxyphenyl methylcarbamate (Propoxur), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 727;
- (35) 1-(3,5-Dichloro-2,4-difluorophenyl)-3-(2,6-difluorobenzoyl)urea (Teflubenzuron), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 790;
- (36) S-tert-butylthiomethyl O,O-dimethyl phosphorodithioate (Terbufos), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 795;
- (37) Ethyl (3-tert.-butyl-1-dimethylcarbamoyl-1H-1,2,4-triazol-5-yl-thio)acetate, (Triazamate), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 1006;
- (38) 2-sec-butylphenyl methylcarbamate (Fenobucarb), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 371;
- (39) N-tert.-Butyl-N'-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide (Tebufenozide), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 943;
- (40) (±)-5-Amino-1-(2,6-dichloro- $\alpha,\alpha,\alpha$ -trifluoro-p-tolyl)-4-trifluoromethyl-sulphonylpyrazole-3-carbonitrile (Fipronil), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 463;

- (41)  $\alpha$ -Cyano-4-fluoro-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate (beta-Cyfluthrin), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 250;
- (42) (4-Ethoxyphenyl)[3-(4-fluoro-3-phenoxyphenyl)propyl](dimethyl)silane (Silaflluofen), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 912;
- (43) tert.-butyl (E)- $\alpha$ -(1,3-dimethyl-5-phenoxy-pyrazol-4-yl-methyleneamino-oxy)-p-toluate (Fenpyroximate), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 450;
- (44) 2-tert.-butyl-5-(4-tert.-butylbenzylthio)-4-chloropyridazin-3(2H)-one (Pyridaben), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 879;
- (45) 4-tert.-butylphenethyl quinazolin-4-yl ether (Fenazaquin), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 426;
- (46) 4-Phenoxyphenyl (RS)-2-(pyridyloxy)propyl ether (Pyriproxyfen), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 887;
- (47) 5-Chloro-N-[2-[4-(2-ethoxyethyl)-2,3-dimethylphenoxy]ethyl]-6-ethylpyrimidine-4-amine (Pyrimidifen), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 887;
- (48) (E)-N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-methyl-2-nitrovinylidenediamine (Nitenpyram), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 736;
- (49) (E)-N'-[(6-chloro-3-pyridyl)methyl]-N<sup>2</sup>-cyano-N<sup>1</sup>-methylacetamidine (NI-25, Acetamiprid), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 730;
- (50) Avermectin B<sub>1</sub> (Abamectin), from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 1;
- (51) An insect-active extract from a plant, especially (2R,6aS,12aS)-1,2,6,6a,12,12a-hexhydro-2-isopropenyl-8,9-dimethoxy-chromeno[3,4-b]furo[2,3-h]chromen-6-one (Rotenono), from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 758; and an extract from *Azadirachta indica*, insbesondere Azadirachtin, from The Pesticide Manual, 10<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 54; and

- (52) A preparation which contains insect-active nematodes, preferably *Heterorhabditis bacteriophora* and *Heterorhabditis megidis*, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 560; *Steinernema feltiae*, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 920, and *Steinernema scapterisci*, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 921;
- (53) A preparation obtainable from *Bacillus subtilis*, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 62; or from a *Bacillus thuringiensis* strain with the exception of compounds isolated from GC91 or from NCTC11821;
- (54) A preparation which contains insect-active fungi, preferably *Verticillium lecanii*, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 1040; *Beauveria brogniartii*, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 69; and *Beauveria bassiana*, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 69;
- (55) A preparation which contains insect-active viruses, preferably Neodiprion Sertifer NPV, from The Pesticide Manual, 9<sup>th</sup>Ed. (1991), The British Crop Protection Council, London, page 616; *Mamestra brassicae* NPV, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 633; and *Cydia pomonella* granulosis Virus, from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 247;
- (179) (Indeno [1,2-e] [1,3,4] oxadiazine-4a (3H)-carboxylic acid, 7-chloro-2,5-dihydro-2-[[[(methoxycarbonyl) [(4-trifluoromethoxy) phenyl] amino] carbonyl]-, methyl ester] (DPX-MP062), from Brighton Crop Protection Conference, 1996, 449- 456;
- (180) N'-tert.-butyl-N'-(3,5-dimethylbenzoyl)-3-methoxy-2-methylbenzohydrazide (RH-2485, Methoxyfenozide), from Brighton Crop Protection Conference, 1996, 481- 486;
- (181) (N'-[4-methoxy-biphenyl-3-yl]-hydrazinecarboxylic acid isopropyl ester (D 2341), from Brighton Crop Protection Conference, 1996, 487- 493;
- (183) Chlorfenapyr from The Pesticide Manual, 10<sup>th</sup>Ed. (1994), The British Crop Protection Council, London, page 209.
- (185) Spinosad is the fermentation product A83543 of *Saccharopolyspora spinosa*, a mixture of macrolide compounds having the main components A83543A and A83543D, and is known from EP-A-375'316.

Compounds (1) to (185) having at least one basic centre may form e.g. acid addition salts. These are formed for example with strong inorganic acids, such as mineral acids, e.g. perchloric acid, sulphuric acid, nitric acid, nitrous acid, a phosphoric acid or a hydrohalic acid, with strong organic carboxylic acids, typically C<sub>1</sub>-C<sub>4</sub>alkanecarboxylic acids substituted where appropriate for example by halogen, e.g. acetic acid, such as dicarboxylic acids that are unsaturated where appropriate, e.g. oxalic, malonic, succinic, maleic, fumaric or phthalic acid, typically hydroxycarboxylic acids, e.g. ascorbic, lactic, malic, tartaric or citric acid, or benzoic acid, or with organic sulphonc acids, typically C<sub>1</sub>-C<sub>4</sub>alkanesulphonic or arylsulphonic acids substituted where appropriate for example by halogen, e.g. methanesulphonic or p-toluenesulphonic acid. Furthermore, compounds (1) to (185) having at least one acidic group may form salts with bases. Appropriate salts with bases are for example metal salts, such as alkali metal salts or alkaline earth metal salts, e.g. sodium, potassium or magnesium salts, or salts with ammonia or with an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, e.g. ethyl, diethyl, triethyl or dimethyl propylamine, or with a mono-, di- or trihydroxy-lower-alkylamine, e.g. mono-, di- or triethanolamine. In addition, corresponding inner salts may optionally be formed. Agrochemically advantageous salts are preferred in the context of the invention. Hereinbefore and hereinafter, compounds (A) and (1) to (185) in free form are to be understood as meaning also their salts, and their salts are to be understood as meaning also the corresponding free compounds (A) and (1) to (185). The same applies to tautomers of compounds (A) and (1) to (185) and their salts. In general, the free form in each case is preferred.

A composition that is preferred in the context of the present invention is one which contains emamectin as an agrochemically compatible salt, especially as the benzoate, substituted benzoate, benzenesulphonate, citrate, phosphate, tartrate or maleate; most preferably as the benzoate or benzenesulphonate, especially the benzoate.

Preference is also given to mixtures which contain emamectin (MK-244) in a mixture ratio of  $B_{1a} > 80\%$  by weight,  $B_{1b} < 20\%$  by weight, especially  $B_{1a} > 90\%$  by weight,  $B_{1b} < 10\%$  by weight.

Preference is given to a composition which contains, in addition to emamectin, only one other pesticidally active compound (1) to (185). Preference is also given to compositions

which contain, in addition to emamectin, fipronil, or pyriproxyfen, or cartap, or diflubenzuron, or imidacloprid, or bensultap, or hexythiazox or spinosad.

Equally preferred are compositions which contain a compound that may be isolated from a strain of *Bacillus thuringiensis*. Of these, those which are especially preferred are the following insecticidally active compounds, or strains from which they may be isolated:

SAN 415I, San 239I, SAN 401I, H7 (B401), H14, EG2348 (Condor OF<sup>®</sup>), EG2349 (Bollgard<sup>®</sup>), EG2371 (Cutlass<sup>®</sup>), EG2424 (Foil<sup>®</sup>, Jackpot<sup>®</sup>); H3a,3b (Javelin<sup>®</sup>, Steward<sup>®</sup>, Thuricide<sup>®</sup>, Vault<sup>®</sup>); CGA237218 (M200, Able<sup>®</sup>), H14, GC91 (Agree<sup>®</sup>, Turex<sup>®</sup>), DSM3435, known from US-P-4,996,156; DSM3440, known from US-P-4,996,156; HD541, HD571 and HD73; more particularly H7 (B401), H14, H3a,3b, CGA237218 (M200), H14, GC91, DSM3435; DSM3440, HD541, HD571 and HD73; especially GC91; H3a,3b; and M200; in particular GC91.

The active ingredient combination according to the invention contains the active ingredient (A) and one of active ingredients (1) to (185) preferably in a mixture ratio of 100:1 to 1:6000, especially 1:50 to 50:1, particularly in a ratio between 1:20 and 20:1, especially between 10:1 and 1:10, most particularly between 5:1 and 1:5, most preferably between 2:1 and 1:2, equally preferably between 4:1 and 2:1, in particular, in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or, 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. These ratios indicate on the one hand ratios by weight, and also on the other hand molar ratios.

It has now surprisingly been found that the combination of emamectin or one of its salts, with one of active ingredients (1) to (185) brings about not only an added enhancement of the spectrum of activity on the pests to be controlled, which was principally expected, but also achieves a synergistic effect, which extends the limits of activity of both preparations in two respects:

On the one hand, the application rates of emamectin and the individual compounds (1) to (185) are lowered whilst retaining good activity. On the other hand, the combined mixture still achieves a high degree of pest control even where both individual substances have

become completely ineffective owing to too low application rates. This allows on the one hand a substantial broadening of spectrum of the controllable pests and on the other hand an increase in safety during usage.

Apart from the actual synergistic effect in respect of the pesticidal activity, the compositions according to the invention also have further surprising advantages, which in a broadened sense can likewise be regarded as synergistic: For example, pests are controlled, which cannot be controlled at all or only with insufficient effect using emamectin or (1) to (185), and the compositions according to the invention show better plant tolerance, typically reduced phytotoxicity, than emamectin or (1) to (185). In addition, the insects can be controlled at their different stages of development, which is in part not the case with emamectin or the individual compounds (1) to (185), since these compounds may be used for example only as adulticides or larvicides against quite specific stages of larvae. Furthermore, combinations of emamectin with certain of compounds (1) to (185) demonstrate more favourable behaviour when grinding, mixing, during storage and also when spraying; they are in certain cases safer in the handling and have favorable ecological properties.

The compositions according to the invention have valuable preventative and/or curative properties in the domain of pest control, at low application rates, whilst having favourable tolerance by warm-blooded animals, fish and plants, and they have a very favourable biocidal spectrum. The compositions according to the invention are active against all or individual stages of development of normally sensitive and also resistant animal pests, such as insects and representatives of the order Acarina. The insecticidal and/or acaricidal activity of the compositions according to the invention may be seen directly, i.e. by the mortality of the pests, which commences immediately or only after some time, for example during a moult, or indirectly, e.g. by reduced egg laying and/or hatching rate, good activity corresponding to a mortality rate of at least 50 to 60%.

The animal pests mentioned include, for example, those that are mentioned in European Patent Application EP-A-736,252. The pests mentioned therein are included by reference thereto in the present subject matter of the invention.

Using the active ingredient mixtures according to the invention, pests of the type mentioned, which appear in particular on plants, especially on crop plants and ornamentals in agriculture, in horticulture and in forestry, or on parts of such plants such as fruits, flowers, foliage, stems, tubers or roots, can be controlled, i.e. stopped or destroyed, whereby parts of the plant which grow later are in part also protected against these pests.

The pesticide mixture according to the invention may be used to advantage for pest control in cereals, such as maize or sorghum; in fruit, e.g. pip, stone and berry fruit, such as apples, pears, plums, peaches, almonds, cherries or berries, e.g. strawberries, raspberries and blackberries; in legumes, such as beans, lentils, peas or soybeans; in oil cultivation, such as rape, mustard, poppy, olives, sunflowers, coconut, castor oil, cacao or peanut; in *Cucurbita* such as squashes, cucumbers or melons; in fibre plants, such as cotton, flax, hemp or jute; in citrus fruits, such as oranges, lemons, grapefruits or mandarin oranges; in vegetables, such as spinach, lettuce, asparagus, cabbage varieties, carrots, onions, tomatoes, potatoes or paprika; in *Lauraceae*, such as avocado, cinnamon or camphor; or in tobacco, nuts, coffee, aubergines, sugar cane, tea, pepper, grapevines, hops, bananas, natural rubber plants, or ornamental plants, in particular in maize, sorghum, pip and stone fruit, legumes, *Cucurbita*, cotton, citrus fruits, vegetables, aubergines, grapevines, hops or ornamental plants, especially in maize, sorghum, apples, pears, plums, peaches, beans, peas, soybeans, olives, sunflowers, coconut, cacao, peanuts, cucumbers, squashes, citrus fruits, cabbage varieties, tomatoes, potatoes, grapevines or cotton, most preferably in grapevines, citrus fruits, apples, pears, tomatoes and cotton.

Further fields of application for the active ingredient mixtures according to the invention are the protection of stock and stores and material, as well as in the hygiene sector, especially the protection of domestic and farm animals from pests of the type mentioned.

The pest control compositions according to the invention may be, depending on the intended objectives and prevailing circumstances, emulsifiable concentrates, suspension concentrates, directly sprayable or dilutable solutions, coatable pastes, diluted emulsions, spray powders, soluble powders, dispersible powders, wettable powders, dusts, granules or encapsulations in polymeric substances which contain emamectin and one of the other active ingredients (1) to (185) according to the invention.

The active ingredients are used in these compositions in pure form, the solid active ingredients, e.g. in a special grain size, or preferably together with - at least - one of the excipients that are usual in formulation techniques, such as diluents, e.g. solvents or solid carrier materials, or such as surface-active compounds (surfactants).

The formulation excipients are for example solid carrier materials, solvents, stabilisers, slow-release excipients, colourings and optionally surface-active substances (surfactants). The carrier materials and excipients include all substances that are customarily employed with plant protection compositions, especially with mollusc control compositions. The excipients in question, such as solvents, solid carrier materials, surface-active compounds, non-ionic surfactants, cationic surfactants, anionic surfactants and further excipients in the compositions according to the invention are, for example, the same as those described in EP-A-736,252; they are included in the present subject matter of the invention by reference thereto.

The compositions normally contain 0.1 to 99%, especially 0.1 to 95%, of a mixture of active ingredient (A) with one of active ingredients (1) to (185), and 1 to 99.9%, especially 5 to 99.9%, of - at least - one solid or liquid excipient, whereby, as a rule, 0 to 25%, especially 0.1 to 20%, of the composition may be surfactants (% indicates percent by weight). While concentrated agents are preferred as commercial products, the final user normally uses diluted agents, which have a substantially lower concentration of active ingredient. Preferred compositions are made up in particular as follows (% = percent by weight):

Emulsifiable concentrates:

active ingredient mixture:	1 to 90%, preferably 5 to 20%
surfactant:	1 to 30%, preferably 10 to 20 %
solvent:	5 to 98%, preferably 70 to 85%

Dusts:

active ingredient mixture:	0,1 to 10%, preferably 0,1 to 1%
solid carrier substance:	99.9 to 90%, preferably 99.9 to 99%



Suspension concentrates:

active ingredient mixture:	5 to 75%, preferably 10 to 50%
water:	94 to 24%, preferably 88 to 30%
surfactant:	1 to 40%, preferably 2 to 30%

Wettable powders:

active ingredient mixture:	0.5 to 90%, preferably 1 to 80%
surfactant:	0.5 to 20%, preferably 1 to 15%
solid carrier substance:	5 to 99%, preferably 15 to 98%

Granules:

active ingredient mixture:	0.5 to 30%, preferably 3 to 15%
solid carrier substance:	99.5 to 70%, preferably 97 to 85%

The compositions according to the invention may also contain further solid or liquid excipients, such as stabilisers, e.g. optionally epoxidised vegetable oils (e.g. epoxidised coconut oil, rapeseed oil or soybean oil), antifoaming agents, e.g. silicone oil, preservatives, viscosity regulators, binding agents and/or tackifiers, as well as fertilizers or other active ingredients to achieve special effects, e.g. bactericides, fungicides, nematocides, molluscicides or herbicides.

The compositions according to the invention are produced in a known manner; with no excipients, this takes place e.g. by grinding, sieving and/or compressing a solid active ingredient or active ingredient mixture, e.g. to a certain grain size; and in the presence of at least one excipient, e.g. by intimately mixing and/or grinding the active ingredient or active ingredient mixture with the excipient(s). The process for the preparation of the composition is therefore a further object of the invention.

The mixtures of emamectin with one or more of compounds (1) to (185) are preferably used with excipients that are usual in formulation techniques and are therefore processed in known manner into emulsifiable concentrates, directly sprayable or dilutable solutions, diluted emulsions, wettable powders, soluble powders, dusts, granules and also encapsulations in e.g. polymeric substances. The application processes, such as spraying, misting, dusting, wetting, sprinkling or pouring, are chosen according to the intended objectives and prevailing circumstances in the same way as for choosing the type of composition.

The application processes for the compositions, i.e. the processes for controlling pests of the type mentioned, to be chosen according to the intended objectives and prevailing circumstances, such as spraying, misting, dusting, coating, dressing, sprinkling, pouring or injection into the plant, and the usage of the compositions for controlling pests of the type mentioned, are further objects of the invention. Typical application rates are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm, of active ingredient. The application rate may vary within a wide range and depends on the constitution of the soil, the type of application (leaf application; seed dressing; application in the seed furrow), the plant being cultivated, the pest to be controlled, the prevailing climatic conditions and other factors determined by the type of application, the time of application and the target culture. The application rates per hectare are generally 1 to 2000 g active ingredient per hectare, especially 10 to 1000 g/ha, preferably 20 to 600 g/ha.

One preferred application process in the field of plant protection is application to the foliage of the plants (leaf application), the frequency of application and the application rate depending on the severity of infestation by the pest in question. However, the active ingredients may also reach the plants through the root system (systemic action), by drenching the locus of the plants with a liquid composition or by adding the active ingredients in solid form to the locus of the plants, e.g. the soil, for example in the form of granules (soil application). In the case of paddy fields, such granules may be dispensed into the flooded rice field.

The compositions according to the invention are also suitable for the protection of plant propagation material, e.g. seed stock, such as fruits, tubers or grain, or plant cuttings, from animal pests. In this instance, the propagation material may be treated with the composition prior to cultivation, e.g. seed stock is dressed prior to sowing. The active ingredients according to the invention may also be applied to seed grain (coating) by either drenching the grains in a liquid composition or coating them with a solid composition. The composition may also be applied when the propagation material is cultivated at the site of cultivation, e.g. when sowing in the seed furrow. This treatment process for plant propagation material and the plant propagation material thus treated are further objects of the invention.

The following examples serve to illustrate the invention. They do not limit the invention.

Formulation Examples (% = percent by weight, ratios of active ingredient = weight ratios)

<u>Beispiel F1: Emulsion concentrates</u>	a)	b)	c)
active ingredient mixture [emamectin:			
compound (1) to (185) = 1 : 3]	25 %	40 %	50 %
Ca dodecyl benzene sulphonate	5 %	8 %	6 %
castor oil polyethylene glycol ether (36 mols EO)	5 %		
tributylphenol polyethylene glycol ether (30 mols EO)		12 %	4 %
cyclohexanone		15 %	20 %
xylene mixture	65 %	25 %	20 %

EO indicates the degree of ethoxylation of castor oil or tributylphenol.

By diluting with water, emulsions of any desired concentration may be produced from such concentrates.

<u>Example F2: Solutions</u>	a)	b)	c)	d)
active ingredient mixture [emamectin:				
compound (1) to (185) = 1 : 10]	80 %	10 %	5 %	95 %
ethylene glycol monomethyl ether		20 %		
polyethylene glycol molecular weight 400	-	70 %		
N-methyl-2-pyrrolidone	20 %	-		
epoxidised coconut oil			1 %	5 %
benzine (boiling limits 160-190°C)			94 %	

The solutions are suitable for usage in the form of the smallest droplets.

<u>Example F3: Granules</u>	a)	b)	c)	d)
active ingredient mixture [Emamectin:				
compound (1) to (185) = 1 : 5]	5 %	10 %	8 %	21 %
kaolin	94 %		79 %	54 %
highly dispersed silicic acid	1 %		13 %	7 %
attapulgate		90 %		18 %

The active ingredients are dissolved together in dichloromethane, sprayed onto the carrier and the solvent then evaporated under vacuum.

It is often more practical to formulate the active ingredient of formula (A) and one of its mixing partners (1) to (185) individually and then to combine them shortly before usage in the applicator in the desired mixture ratio as a tank mixture in water.

Biological Examples (% = percent by weight, if not otherwise stated)

There is always a synergistic effect if the effect  $We$  of the combination of an active ingredient of formula (A) with one of active ingredients (1) to (185) is greater than the sum of effects of the active ingredients applied individually:

$$We > X + Y \quad (B)$$

The pesticidal activity  $We$  to be expected for a given combination of two pesticides may however also be calculated as follows (see COLBY, S.R., "Calculating synergistic and antagonistic response of herbicide combinations", Weeds 15, pages 20-22, 1967):

$$We = X + \frac{Y (100 - X)}{100} \quad (C)$$

In this formula:

$X$  = percentage mortality when treating with emamectin at an application rate of  $p$  kg per hectare compared with the untreated control (= 0 %).

$Y$  = percentage mortality when treating with one compound (1) to (185) at an application rate of  $q$  kg per hectare compared with the untreated control.

$We$  = expected pesticidal activity (percentage mortality compared with untreated control) after treatment with emamectin and one compound (1) to (185) at an application rate of  $p + q$  kg active ingredient per hectare.

If the effect actually observed is greater than the value  $We$  expected, there is synergism.

Example B1: Activity against *Bemisia tabaci*

Bush bean plants are placed in gauze cages and colonised with adult *Bemisia tabaci*. After egg laying has taken place, all adults are removed. 10 days later, the plants with the nymphs found thereon are sprayed with an aqueous suspension spray mixture containing 50 ppm of

the active ingredient mixture. After a further 14 days, the percentage of eggs that have hatched is evaluated and compared with untreated control batches.

In this test, the combinations of emamectin with one of active ingredients (1) to (185) show a synergistic effect. Good activity is shown in particular by a suspension spray mixture containing 40 ppm of emamectin and 10 ppm of compound (2).

Example B2: Activity against *Spodoptera littoralis* grubs

Young soybean plants are sprayed with an aqueous emulsion spray mixture containing 360 ppm of the active ingredient mixture. After the spray coating has dried on, the soybean plants are colonised with 10 grubs of the third stage of *Spodoptera littoralis* and placed in a plastic container. Evaluation takes place 3 days later. The percentage reduction in population or percentage reduction in feeding damage (% activity) is determined by comparing the number of dead grubs and the feeding damage on the treated plants with those on the untreated plants.

In this test, the combinations of emamectin with one of active ingredients (1) to (185) show a synergistic effect. In particular, a suspension spray mixture containing 200 ppm of emamectin and 160 ppm of compound (2) and a suspension spray mixture containing 180 ppm of emamectin and 180 ppm of compound (XV) show good activity.

Example B3: Ovicidal activity on *Lobesia botrana*

Eggs of *Lobesia botrana* deposited on filter paper are immersed for a short time in an acetonic-aqueous test solution containing 400 ppm of the active ingredient mixture to be tested. After the test solution has dried on, the eggs are incubated in Petri dishes. After 6 days, the percentage of eggs that have hatched is evaluated and compared with untreated control batches (% hatching reduction).

In this test, the combinations of emamectin with one of active ingredients (1) to (185) show a synergistic effect. In particular, a suspension spray mixture containing 300 ppm of emamectin and 100 ppm of compound (3) and a suspension spray mixture containing 200 ppm of emamectin and 200 ppm of compound (16) show good activity.

Example B4: Ovicidal activity on *Heliothis virescens*

Eggs of *Heliothis virescens* deposited on filter paper are immersed for a short time in an acetonic-aqueous test solution containing 400 ppm of the active ingredient mixture to be tested. After the test solution has dried on, the eggs are incubated in Petri dishes. After 6 days, the percentage of eggs that have hatched is evaluated and compared with untreated control batches (% hatching reduction).

In this test, the combinations of emamectin with one of active ingredients (1) to (185) show a synergistic effect. In particular, a suspension spray mixture containing 240 ppm of emamectin and 160 ppm of compound (12) and a suspension spray mixture containing 300 ppm of emamectin and 100 ppm of compound (5) show good activity.

Example B5: Activity against *Plutella xylostella* grubs

Young cabbage plants are sprayed with an aqueous emulsion spray mixture containing 440 ppm of the active ingredient. After the spray coating has dried on, the cabbage plants are colonised with the third stage of *Plutella xylostella* and added to a plastic container. Evaluation takes place 3 days later. The percentage reduction in population or percentage reduction in feeding damage (% activity) is determined by comparing the number of dead grubs and the feeding damage on the treated plants with those on the untreated plants.

In this test, the combinations of emamectin with one of active ingredients (1) to (185) show a synergistic effect. In particular, a suspension spray mixture containing 400 ppm of emamectin and 40 ppm of compound (7) and a suspension spray mixture containing 220 ppm of emamectin and 220 ppm of compound (4) show good activity.

What is claimed is:

1. Composition for the control of insects or representatives of the order *Acarina*, which is characterised in that it contains a quantitatively variable combination of emamectin (A) in free form or in salt form, as well as one or more of the compounds

Aldicarb; Azinphos-methyl; Benfuracarb; Bifenthrin; Buprofezin; Carbofuran; Carbosulfan; Cartap; Chlorfluazuron; Chlorpyrifos; Cyfluthrin; Lambda-Cy-halothrin; Alpha-cypermethrin; zeta-Cypermethrin; Deltamethrin; Diflubenzuron; Endosulfan; Ethiofencarb; Fenitrothion; Fenobucarb; Fenvalerate; Formothion; Methiocarb; Heptenophos; Imidacloprid; Isoprocarb; Methamidophos; Methomyl; Mevinphos; Parathion; Parathion-methyl; Phosalone; Pirimicarb; Propoxur; Teflubenzuron; Terbufos; Triazamate; Fenobucarb; Tebufenozide; Fipronil; beta-Cyfluthrin; Silafluofen; Fenpyroximate; Pyridaben; Fenazaquin; Pyriproxyfen; Pyrimidifen; Nitenpyram; NI-25, Acetamiprid; Avermectin; an insect-active extract from a plant; a preparation which contains insect-active nematodes; a preparation obtainable from *Bacillus subtilis*; a preparation which contains insect-active fungi; a preparation which contains insect-active viruses; AC 303 630; Acephat; Acrinathrin; Alanycarb; Alphamethrin; Amitraz; AZ 60541; Azinphos A; Azinphos M; Azocyclotin; Bendiocarb; Bensultap; Betacyfluthrin; BPMC; Brofenprox; Bromophos A; Bufencarb; Butocarboxim; Butylpyridaben; Cadusafos; Carbaryl; Carbopheno-thion; Chloethocarb; Chlorethoxyfos; Chlormephos; Cis-Res-methrin; Clocythrin; Clofentezin; Cyanophos; Cycloprothrin; Cyhexatin; Demeton M; Demeton S; Demeton-S-methyl; Dichlofenthion; Dicliphos; Diethion; Dimethoat; Dimethylvinphos; Dioxathion; Edifenphos; Esfenvalerat; Ethion; Ethofenprox; Ethoprophos; Etrimphos; Fenamiphos; Fenbutatinoxid; Fenothiocarb; Fenpropathrin; Fenpyrad; Fenthion; Fluazinam; Flucycloxuron; Flucythrinate; Flufenoxuron; Flufenprox; Fonophos; Fosthiazat; Fubfenprox; HCH; Hexaflumuron; Hexythiazox; Iprobenfos; Isafenphos; Isoxathion; Ivermectin; Lambda-cyhalothrin; Malathion; Mecarbam; Mesulfenphos; Metaldehyd; Metolcarb; Milbemectin; Moxidectin; Naled; NC 184; Omethoat; Oxamyl; Oxydemethon-methyl; Oxydeprofos; Permethrin; Phenthoat; Phorat; Phosmet; Phoxim; Pirimiphos M; Pirimiphos A; Promecarb; Propaphos; Prothiofos; Prothoat; Pyrachlophos; Pyrada-phenthion; Pyresmethrin; Pyrethrum; RH 5992; Salithion; Sebufos; Sulfotep; Sulprofos; Tebufenpyrad; Tebupirimphos; Tefluthrin; Temephos; Terbam; Tetrachlor-vinphos; Thiafenox; Thiodicarb; Thiofanox; Thionazin; Thuringiensin; Tralomethrin; Triarthen; Triazophos; Triazuron; Trichlorfon; Triflumuron; Trimethacarb; Vamidothion; Xylilcarb; YI 5301/5302; Zetamethrin;

DPX-MP062; RH-2485; D 2341; XMC (3,5,-Xy-lyl Methylcarbamate); Chlorfenapyr; or Spinosad,

in free form or in salt form, and at least one excipient.

2. Composition according to claim 1, which contains emamectin as the benzoate.
3. Composition according to claim 1, which contains Fipronil.
4. Composition according to claim 1, which contains Pyriproxyfen.
5. Composition according to claim 1, which contains Cartap.
6. Composition according to claim 1, which contains Spinosad.
7. Process for the control of pests, whereby a composition such as that described in claims 1 to 6 is applied to the pests or to their locus.
8. Process according to claim 7 for the protection of plant propagation material, whereby the propagation material or the site at which the propagation material is cultivated is treated.
9. Process for the preparation of a composition containing at least one excipient, as described in one of claims 1 to 6, whereby the active ingredients are intimately mixed with the excipient(s).
10. Plant propagation material, treated according to the process described in claim 8.
11. Use of a composition such as that described in claims 1 to 6 in a process such as that described in one of claims 7 or 8.
12. Use of emamectin or a salt thereof in the preparation of a composition such as that described in one of claims 1 to 6.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/04656

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N43/90 //(A01N43/90,47:24,57:16,47:10,53:00,47:34,37:34,  
43:56,43:40,43:22)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 99 25187 A (NOVARTIS AG) 27 May 1999 (1999-05-27) the whole document	1-12
X	GB 2 220 856 A (MERCK & CO INC) 24 January 1990 (1990-01-24) the whole document	1-12
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 October 1999

Date of mailing of the international search report

21.12.99

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/04656

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE STN [Online]  MICINSKI, S. ET AL.: "Efficacy of selected insecticide mixtures for bollworm/tobacco budworm control, 1996"  retrieved from BIOSIS, accession no. 1997:417260, Document no. PREV199799716463  XP002900695  abstract  &amp; SAXENA, C.R. ARTNROPOD MANAGEMENT TESTS, 1996,  vol. 22, 1997, pages 261-262,  ---</p>	1-12
X	<p>DATABASE STN [Online]  LEIBEE, GARY L. ET AL.: "Efficacy of emamectin benzoate and Bacillus thuringiensis at controlling diamondback moth (Lepidoptera: Plutellidae) populations on cabbage in Florida"  retrieved from CAPLUS, accession no. 1995:523270, Document no. 122:284557  XP002900696  abstract  &amp; FLA. ENTOMOL.,  vol. 78, no. 1, 1995, pages 82-96,  ---</p>	1-12
P,X	<p>WO 99 18796 A (RHONE-POULENC AGRO)  22 April 1999 (1999-04-22)  page 5, line 13 - line 22; claims  ---</p>	1-12
A	<p>DATABASE WPI  Section Ch, Week 198451  Derwent Publications Ltd., London, GB;  Class C03, AN 1984-316303  XP002900697  &amp; JP 59 199616 A (SUMITOMO CHEM CO LTD),  12 November 1984 (1984-11-12)  abstract  -&amp; JP 59 199616 A (SUMITOMO KAGAKU KOGYO KK) 12 November 1984 (1984-11-12)  ---</p>	1-12
A	<p>DATABASE WPI  Section Ch, Week 198549  Derwent Publications Ltd., London, GB;  Class C02, AN 1985-307652  XP002900698  &amp; JP 60 214715 A (SUMITOMO CHEM IND KK),  28 October 1985 (1985-10-28)  abstract  -&amp; JP 60 214715 A (SUMITOMO KAGAKU KOGYO KK) 28 October 1985 (1985-10-28)  ---</p>	1-12
A	<p>WO 98 27817 A (BAYER AG)  2 July 1998 (1998-07-02)  ---</p>	1-12
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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/04656

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 242 502 A (HOECHST AG)</p> <p>28 October 1987 (1987-10-28)</p> <p>-----</p>	1-12

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 99/04656

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 99/04656

Several compositions for the control of insects or representatives of the order Acarina which contain a quantitatively variable combination of emamectin (A) in free form or in salt form, as well as one or more of the compounds "Aldicarb" (2) to "Spinosad" (185) in free form or in salt form, and at least one excipient as described in claims 1-6 and corresponding processes, plant propagation material and uses as described in claims 7-12.

The compounds (2) to (185) represent members of a plurality of classes having no common structure. Confer PCT Rule 13.2. Some of the compounds (2) to (185) may inter alia be identified as

1) carbamates such as Aldicarb, Benfuracarb, Carbofuran, Carbosulfan, Cartap, Ethiofencarb, Fenobucarb (BPMC), Methiocarb, Isoprocarb, Primicarb, Propoxur, Triazamate, Bendiocarb, Metolcarb, Oxamyl, Fenothiocarb, Xylilcarb, Chloethocarb, Trimethacarb and XMC (3,5,-Xylil Methylcarbamate)

2) organophosphates such as Azinphos-methyl, Chlorpyrifos, Fenitrothion, Formothion, Heptenophos, Methamidophos, Mevinphos, Parathion, Parathion-methyl, Phosalone, Terbufos, Azinphos A, Azinphos M, Dimethylvinphos, Edifenophos, Ethoprophos, Etrimphos, Fenamiphos, Fonophos, Iprobenfos, Isofenphos, Malathion, Phosmet, Pirimphos M, Propaphos, Prothiofos, Suprofos, Tetrchlor-vinphos, Triazophos, Omethoat, Oxydemethon-methyl, Fenthion, Oxydeprofos, Prothoat, Tebupirimphos, Temephos, Cyanophos, Acephate, Ethion and Trichlorfon

3) pyrethroids such as Bifenthrin, Cyfluthrin, Lambda-Cyhalothrin, Alpha-Cypermethrin, Zeta-Cypermethrin, Deltamethrin, Fenvalerate, Beta-Cyfluthrin, Acrinathrin, Alphamethrin, Cis-Res-methrin, Clocythrin, Esfenvalerat, Permethrin, Pyresmethrin, Pyrethrum, Tefluthrin, Talomethrin and Zetamethrin

4) thiadiazines such as Buprofezin

5) benzoylureas such as Chlorfluazuron, Diflubenzuron, Teflubenzuron, Flucycloxuron, Flufenoxuron and Triflumeron

6) organochlorines such as Endosulfan and HCH

7) nitroimidazolidinylideneamines such as Imidacloprid

8) carbamoyloximes such as Methomyl and Thiodicarb

9) macrolides such as Avermectin, Milbemectin, Moxidectin and Ivermectin

10) organotins such as Cyhexatin, Fenbutatin oxid and Azocyclotin

11) amidines such as Amitraz

12) carboxamides such as Fenpyrad and Tebufenpyrad

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 99/04656

- 13) an insect-active extract from a plant
- 14) a preparation which contains insect-active nematodes
- 15) a preparation obtainable from *Bacillus subtilis*
- 16) a preparation which contains insect-active fungi
- 17) a preparation which contains insect-active viruses
- 18) phenyl ethers such as Pyriproxifen
- 19) a sulphonylpyrazole such as Fipronil
- 20) a macrolide such as Spinosad
- 21) carbamoyloximes such as Thiodicarb
- 22) isothiazolidinones such as Hexythiazox

# INTERNATIONAL SEARCH REPORT

Information on patent family members

28/09/99

International application No.

PCT/EP 99/04656

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Information on patent family members

28/09/99

International application No.

PCT/EP 99/04656

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